DEGENERACY IN IDEAL CHEMICAL EQUILIBRIUM PROBLEMS

BY

JAMES H. BIGELOW

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CONTENTS

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EQUILIBRIUM PROBLEMS

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I. INTRODUCTION

A single- or multi-phase chemical equilibrium problem may be thought of as the problem of minimizing a particular nonlinear function (the free energy) of composition subject to the conditions that the composition vector be nonnegative and satisfy a system of linear equations ~~(the mass balance~~ laws). It was pointed out in a previous paper (AD-706 018) ~~[1]~~ that the free energy is convex and homogeneous of degree one, but that as a variable approaches zero, the free energy may behave badly.

In this paper, the second in a series of three**, the phrase "chemical equilibrium problem" refers only to a problem with a particular mathematical form. Problems of this form arise in many situations that are not classically denoted chemical equilibrium problems. For example,

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**The first is "Chemistry, Kinetics and Thermodynamics;" the third, "Computing Equilibrium Compositions of Ideal Chemical Systems".

the dual to a geometric programming problem [2], [3], has this form. Also, steady-state problems [4], many of which arise naturally in industry and in the chemical laboratory, can often be represented mathematically by problems of this form.

We call the problems under consideration "ideal" because they are derived from chemical equilibrium problems which take the simplest form possible. As a consequence, the free-energy function is as simple as it can be [1].

The ideal chemical equilibrium problem, then, is the problem of minimizing a function $F(x_1, x_2, \ldots, x_n)$, definded below, subject to the linear constraints:

$$\text{(I.1)} \qquad \sum_{j=1}^{n} a_{ij}x_j = b_i \qquad , i = 1, 2, \ldots, m$$

and the inequalities:

$$\text{(I.2)} \qquad x_j \geq 0, \qquad , j = 1, 2, \ldots, n.$$

The a_{ij} and b_i are given real constants. We assume that the m equations (I.1) are linearly independent, and so that the problem will not be trivial, that $m < n$.

The n variables x_j are partitioned into p nonempty subsets called <u>compartments</u>, or <u>phases</u>. We denote the compartment containing the $j^{\underline{th}}$ variable by $\langle j \rangle$. We may indicate that x_j and x_k are in the same compartment by writing:

$$j \in \langle k\rangle \quad \text{or} \quad k \in \langle j\rangle \quad \text{or} \quad \langle j\rangle = \langle k\rangle.$$

Each compartment has associated with it a sum,

(I.3) $$\bar{x}_{\langle k\rangle} = \sum_{j \in \langle k\rangle} x_j.$$

Each variable has associated with it a variable fraction,

(I.4) $$\hat{x}_j = \frac{x_j}{\bar{x}_{\langle j\rangle}} .$$

The objective function to be minimized is:

(I.5) $$F(x_1, \ldots, x_n) = \sum_{j=1}^{n} x_j(c_j + \log \hat{x}_j).$$

The quantities $c_1, c_2, \ldots, c_n$ are given real constants.

If $x_j = 0$ for some j, then either $\hat{x}_j = 0$ (in the event that $\bar{x}_{\langle j\rangle} > 0$) or $\hat{x}_j$ is undefined (if $\bar{x}_{\langle j\rangle} = 0$). In either case, $\log \hat{x}_j$ is undefined; but to maintain the continuity of F at the boundary of the constraint set, we define $x_j \log \hat{x}_j = 0$ whenever $x_j = 0$ ([5], p. 364).

It will be convenient to use matrix notation. We let A be a matrix whose ij^{th} element is a_{ij}. (The first index refers to the row number, the second to the column. Thus A has m rows and n columns.) Similarly, b is a column vector of dimension m, whose i^{th} component is b_i.

In the same fashion, we let x be the n-vector with components x_j; $\hat{x}$ the n-vector with components $\hat{x}_j$; log $\hat{x}$ the n-vector with components $\log \hat{x}_j$; and c the n-vector with components c_j. All of these are column vectors.

Using vector notation, we may write the chemical equilibrium problem in the following compact form:

$$\begin{aligned} \text{Min } F(x) &= \text{Min } x \cdot (c + \log \hat{x}) \\ \text{s.t.} \quad Ax &= b \\ x &\geq 0. \end{aligned} \tag{I.6}$$

The notation $x \cdot (c + \log \hat{x})$ denotes the inner product of the vectors x and $(c + \log \hat{x})$.

As we shall see, the singular behavior of F at the boundary of its domain, the nonnegative orthant, makes it difficult even to recognize a solution to (I.6). In this paper we discuss a method for surmounting this problem, called degeneracy, and a method for avoiding it.

II. VIRTUAL MOLE FRACTIONS

In this section we will discover how to recognize when a vector x is a solution to Problem (I.6). We touched on this question in [1], where we showed a way to recognize whether x solved (I.6) if x were strictly positive. In this section we extend the result to include all feasible x.

It will be convenient to define the concept of an admissible direction.

Definition: Let a composition vector x be feasible in a given chemical equilibrium problem. That is, x satisfies $Ax = b$, $x \geq 0$. An n-vector θ is said to be admissible at x if for every $t > 0$, t sufficiently small, $x + t\theta$ is feasible.

We will have occasion to consider several different chemical equilibrium problems with different constraint sets. When we refer to the concept of admissibility, we mean that a direction θ is admissible for the problem then under consideration.

Note that θ is admissible at x if and only if $A\theta = 0$ and $\theta_j \geq 0$ for every j such that $x_j = 0$.

The difficulty in recognizing solutions arises from the behavior of the Gibbs function F(x) when some of the

$x_j = 0$. It is well known that since $F(x)$ is convex, F achieves a minimum at x if and only if for every reaction vector θ admissible at x,

$$F'_{\theta}(x) \geq 0$$

where $F'_{\theta}(x)$ is the derivative of F at x in the direction θ. This derivative is linear in θ whenever $x > 0$; but it may be non-linear--indeed it may be infinite--when some $x_j = 0$.

Much of the content of this chapter was anticipated by N. Z. Shapiro, who proved a restricted form of the main theorem, II.4. Theorem II.4 in all its generality was proved by the late Dr. Jon Folkman, although the present author never saw that proof. The proof appearing here is original with the author.

It will be convenient at this point to define two sets.

$$H(A, b) = \{x \in E^n | Ax = b, \quad x \geq 0\}$$

$$M(F|H(A, b)) = \{x \in H(A, b) | F(x) \leq F(y) \,\forall\, y \in H(A, b)\}.$$

(One might as easily define $M(F|W)$ for a general set W and general function $F: W \to E^1$. Thus $M(F|W) = \{x \in W | F(x) \leq F(y)$ $\forall\, y \in W\}$.) Then $H(A, b)$ is the set of all x which satisfy both the mass balance and non-negativity constraints of problem (I.6), i.e., $H(A,b)$ is the set of feasible compositions of the chemical system. $M(F|H(A, b))$ (written $M(F|H)$ if there will be no confusion) is the set of solutions to problem (I.6), and hence the set of equilibrium compositions of the chemical system.

In this section we will derive a characterization of $M(F|H)$. The name, "Virtual Mole Fractions," arises from the fact that in equilibrium chemistry it is convenient to express the variables in units of "moles" and to call the variable fractions "mole fractions." It may happen that at equilibrium, one or more phases of a chemical system are empty. In this case, the mole fractions of the variables in the vanished phases are undefined; but we will show how to define quantities to take their place, quantities called "virtual mole fractions."

Before we can do any of the real work of this section we must satisfy ourselves that Problem (I.6) may be solved using Lagrange multipliers.

<u>Theorem II.1</u>: Assume there exists $x \in H(A, b)$ such that $x > 0$, and suppose that $M(F|H(A, b))$ is nonempty. Let $R = \{x \in E^n | x \geq 0\}$. Then there exists $\pi^o \in E^m$ such that:

$$M(F|H(A, b)) \subset M(F(x) - \pi^o(Ax - b)|R).$$

<u>Remark:</u> This statement says exactly that each solution of (I.6) must also minimize the Lagrangian form $F(x) - \pi^o(Ax - b)$ among all non-negative x.

<u>Proof:</u> From [5], Theorem 8.13, p. 368, we know that F is convex on R. Hence, the Lagrangian is convex.

Let $x^o \in M(F|H(A, b))$ (which we assumed was nonempty), and define the compact, convex set $R_1 = \{x \geq 0 | \|x^o - x\| \leq 1\}$.

From [6], Theorem 6, p. 478, we know that there exists $\pi^o \in E^m$ such that:

$$\text{(II.1)} \qquad F(x^o) = \operatorname*{Min}_{x \in R_1} [F(x) - \pi^o(Ax - b)].$$

Suppose $F(x^1) < F(x^o)$ for some $x^1 \in R$. By choosing $1 \geq \lambda > 0$ sufficiently small we may construct $y = (\lambda x^1 + (1 - \lambda)x^o) \in R_1$, which by convexity must satisfy $F(y) < F(x^o)$. Thus:

$$\text{(II.2)} \qquad F(x^o) = \operatorname*{Min}_{x \in R} [F(x) - \pi^o(Ax - b)].$$

The result is immediate. Q.E.D.

For any $x \geq 0$ we partition the indices $\{1, 2, \ldots, n\}$ into two disjoint sets:

$$I = \{j \mid \bar{x}_{<j>} = 0\}$$

$$J = \{j \mid \bar{x}_{<j>} > 0\}.$$

Given any vector $\theta \in E^n$, we separate it into two terms, θ_I and θ_J,

$$(\theta_I)_j = \begin{cases} \theta_j & \text{if } j \in I \\ 0 & \text{otherwise} \end{cases}$$

$$\theta_J = \theta - \theta_I .$$

With the above notation, we may use [5], Theorems 8.10 and 8.11, p. 368, and the vector notation developed in section I to write the derivative of F at x in the direction θ in the following compact form:

(II.3) $F'_\theta(x) = \theta_I \cdot (c_I + \log \hat{\theta}_I) + \theta_J \cdot (c_J + \log \hat{x}_J)$.

This is defined for all θ admissible at x. We understand that $F'_\theta(x)$ may take on the value $-\infty$. Thus if for some $j \in J$ we have $x_j = 0$, we see that $\log \hat{x}_j = -\infty$. In this case, $\theta_j > 0$ implies that $F'_\theta(x) = -\infty$.

Theorem II.2: Let $x \in H(A, b)$. Then $x \in M(F|H)$ if and only if $F'_\theta(x) \geq 0$ for all θ admissible at x.

Proof: [5], Theorem 10.2, p. 372.

QED.

Corollary II.3: Let $x \in H(A, b)$ and $x > 0$. Then $x \in M(F|H)$ if and only if:

(II.4) $$\theta \cdot (c + \log \hat{x}) = 0 \;\forall\; \theta \ni A\theta = 0.$$

Proof: [5], Theorem 10.3, p. 372. This also follows immediately from Theorem II.2, since $x > 0$ implies I is empty.

QED.

Notice that if $x \in H(A, b)$, and $x > 0$, the optimality condition in Corollary II.3 requires a knowledge only of $\hat{x}$, not of x. It is the mole fractions, not the moles that count. In the event that I is not empty, we would like something to take the place of $\hat{x}$ in (II.4). This motivates the following definition and theorem.

(II.5a) $\hat{\Phi}(x) = \{\varphi \in E^n \mid \varphi > 0,\ \theta\cdot(c + \log \varphi) = 0 \quad \forall\, \theta \ni A\theta = 0,$
$\qquad\qquad$ and $\varphi_j = \hat{x}_j \quad \forall \; j \in J.\}$

Elementary linear algebra shows that we may write the equivalent definition:

(II.5b) $\hat{\Phi}(x) = \{\varphi \in E^n \mid \varphi > 0,\ c + \log \varphi = A^T\pi$ for some $\pi \in E^m,$
$\qquad\qquad$ and $\varphi_j = \hat{x}_j \quad \forall \; j \in J.\}$

<u>Theorem II.4</u>: Assume $\exists\, y \in H(A, b) \ni y > 0$, and let $x \in H(A, b)$. Then $x \in M(F|H)$ if and only if $\exists\, \varphi \in \hat{\Phi}(x) \ni \bar{\varphi}_{<j>} \leq 1$ for every $<j>$, where $\bar{\varphi}_{<j>} = \sum_{k\in<j>} \varphi_k$.

To prove Theorem II.4, we will need the following lemma.

<u>Lemma II.5</u>: Let $\varphi \in E^p$ satisfy $\varphi > 0$. Then for any $\theta \in E^p$, $\theta \geq 0$,

$$\text{(II.6)} \quad \sum_{j=1}^{p} \theta_j \left(\log\left(\frac{\theta_j}{\sum_{k=1}^{p} \theta_k}\right) - \log \varphi_j\right) \geq -\sum_{j=1}^{p} \theta_j \left(\log \sum_{k=1}^{p} \varphi_k\right)$$

<u>Proof:</u> Let $\bar{\theta} = \sum_{k=1}^{p} \theta_k$, $\bar{\varphi} = \sum_{k=1}^{p} \varphi_k$, $\hat{\theta}_j = \frac{\theta_j}{\bar{\theta}}$, $\hat{\varphi}_j = \frac{\varphi_j}{\bar{\varphi}}$

Rearranging terms in (II.6) we find it equivalent to:

$$\text{(II.7)} \qquad \sum_{j=1}^{p} \theta_j \left(\log \hat{\theta}_j - \log \hat{\varphi}_j\right) \geq 0.$$

This function of θ is of exactly the same form as Gibbs function, with $c_j = -\log \hat{\varphi}_j$. If we minimize the function in (II.7) subject only to the constraint $\theta \geq 0$, we will be solving a chemical equilibrium problem. The absence of mass balance constraints tells us that every vector $v \in E^p$ is a reaction vector.

Let $\theta > 0$, and take the derivative in the direction v. By (II.3) this becomes:

$$F_v'(\theta) = \sum_{j=1}^{p} v_j(\log \hat{\theta}_j - \log \hat{\phi}_j)$$

Clearly this is non-negative for every $v \in E^p$ if and only if for each j,

$$\hat{\theta}_j = \hat{\phi}_j .$$

Thus the function is minimized if and only if for some $\alpha \geq 0$, $\theta = \alpha\varphi$.

But clearly $\hat{\theta} = \hat{\phi}$ implies that (II.7) is zero. Q.E.D.

Proof of Theorem II.4: Define the Lagrangian problem $P(\pi)$ to be:

$$\text{(II.8)} \quad P(\pi): \quad \text{Min } G(x) = \text{Min } [F(x) - \pi(Ax - b)]$$
$$\text{s.t. } x \geq 0.$$

Let $x^o \in H(A,b)$. By Theorem II.1, it will be sufficient to show that the following statements are equivalent:

(i) $\exists \; \varphi \in \Phi(x^o) \ni \overline{\varphi}_{<j>} \leq 1 \; \forall <j>$

(ii) $\exists \; \pi^o \in E^m \ni x^o$ solves $P(\pi^o)$.

Note that for each π, $P(\pi)$ is just a chemical equilibrium problem with no linear equality constraints. Thus by Theorem II.2, x^o solves $P(\pi^o)$ if and only if

$$\text{(II.9)}\quad G_\theta'(x^o) = \theta_I\cdot(c_I + \log \hat{\theta}_I) + \theta_J\cdot(c_J + \log \hat{x}_J^o) - \theta\cdot A^T\pi^o \geq 0$$

$$\forall \theta \text{ admissible at } x^o.$$

Clearly, θ is admissible at x^o in this problem if and only if $\theta_j \geq 0$ whenever $x_j^o = 0$. Immediately we see that if $x_j^o = 0$ for some $j \in J$, we can find θ with $\theta_j > 0$, and force $G_\theta'(x^o) = -\infty$. Thus we may suppose $x_j > 0$ for each $j \in J$.

It is obvious that (II.9) cannot hold unless,

$$\text{(II.10)}\qquad c_J + \log \hat{x}_J^o = A_J^T\pi^o .$$

If we define a vector φ by:

$$\text{(II.11)}\qquad c + \log \varphi = A^T\pi^o.$$

then clearly, since $x_j^o > 0$ for $j \in J$, $\varphi \in \Phi(x^o)$. (See definition (II.5b).) Substituting (II.11) into the inequality (II.9), we find that x^o solves $P(\pi^o)$ if and only if:

$$\text{(II.12)}\qquad \theta_I\cdot(\log \hat{\theta}_I - \log \varphi_I) \geq 0 \qquad \forall\ \theta_I \geq 0.$$

Let I^* be the set of compartments $\langle j \rangle$ whose indices are in I. Then (II.12) becomes:

$$\text{(II.13)}\qquad \sum_{\langle k\rangle \in I^*} \left(\sum_{j\in\langle k\rangle} \theta_j(\log \hat{\theta}_j - \log \varphi_j)\right) \geq 0 \qquad \forall\ \theta_I \geq 0.$$

Lemma II.5 considered exactly such quantities as the inner sum. Thus (II.13) holds if and only if:

$$-\sum_{\langle k\rangle \in I^*} \sum_{j \in \langle k\rangle} \theta_j \log \overline{\varphi}_{\langle k\rangle} \geq 0 \qquad \forall\ \theta_I \geq 0.$$

It is easy to see that this is true $\forall\ \theta_I \geq 0$ if and only if

(II.14) $$\overline{\varphi}_{\langle k\rangle} \leq 1 \qquad \forall\ \langle k\rangle \in I^* .$$

Since $\varphi_J = \hat{x}_J^{\,o}$, and $\sum_{j \in \langle k\rangle} \hat{x}_j^{\,o} = 1$ if $k \in J$,

(II.14) holds if and only if statement (i) above is true, completing the proof. Q.E.D.

For each $x \in M(F|H)$, we may define a subset of $\Phi(x)$ as follows:

(II.15) $$\Phi^*(x) = \{\varphi \in \Phi(x) \mid \overline{\varphi}_{\langle j\rangle} \leq 1 \quad \forall \langle j\rangle\}.$$

We call $\Phi^*(x)$ the set of <u>virtual mole fractions</u> associated with x.

There is no reason to suppose that $M(F|H)$ consists of but one point. Problems exist which possess no solution, and others can be constructed which possess many. However, whenever $M(F|H)$ is non-empty and $H(A, b)$ contains a $y > 0$, we can prove uniqueness of a sort.

Theorem II.6: Suppose $\exists\, z \in H(A, b) \ni z > 0$. Then for any $x, y \in M(F|H)$, $\delta^*(x) = \delta^*(y)$. That is, there is a unique set δ^* of virtual mole fractions associated with problem (I.6).

Proof: Define the carrier of a vector $x \in E^n$, $x \geq 0$ by:

$$C(x) = \{j | x_j > 0\} .$$

Earlier in this section we defined a set J of indices of variables in compartments which did not vanish, and in the course of Theorem II.4 argued that if $x \in M(F|H)$, then $j \in J \Rightarrow x_j > 0$. Thus for $x \in M(F|H)$, $J = C(x)$.

Lemma 9.7, pg. 370 of [5] states that if $M(F|H)$ is non-empty, then there exists $x^o \in M(F|H)$ such that:

$$C(x) \subseteq C(x^o) \qquad \forall\, x \in M(F|H) .$$

From this and [5] Lemma 9.5, pg. 370, (which states that if $x, y \in M(F|H)$, then $\hat{x}_j = \hat{y}_j$ whenever both are defined) we know that for every $x \in M(F|H)$,

(II.16) $$\hat{x}_j = \hat{x}_j^o \qquad \forall\, j \in C(x) .$$

Clearly, then,

(II.17) $$\delta^*(x^o) \subseteq \delta^*(x) \qquad \forall\, x \in M(F|H) .$$

Suppose $\omega \in \delta^*(x)$. Let $\theta = x^o - x$. Let us now evaluate $F'_\theta(x)$. We may do this since clearly $\theta_j \geq 0$ if $x_j = 0$, and hence θ is admissible at x. Further, $x, x^o \in M(F|H)$. Thus:

$$\text{(II.18)}\quad F'_\theta(x) = \sum_{j\in C(x)} \theta_j\cdot(c_j + \log \hat{x}_j)$$

$$+ \sum_{j\in C(x^o)-C(x)} \theta_j\,(c_j + \log \hat{\theta}_j) = 0.$$

On the other hand, $\varphi \in \Phi^*(x)$ tells us that:

$$\text{(II.19)}\qquad \sum_{j\in C(x^o)} \theta_j(c_j + \log \varphi_j) = 0\ .$$

Subtracting (II.18) from (II.19) we find that:

$$\text{(II.20)}\qquad 0 = \sum_{j\in C(x^o)-C(x)} \theta_j\,(\log \varphi_j - \log \hat{\theta}_j)$$

$$\leq \sum_{j\in C(x^o)-C(x)} \theta_j \log \bar{\varphi}_{<j>} \leq 0.$$

The first inequality holds as an equality if and only if $\hat{\theta}_j = \varphi_j$ for each j, by Lemma II.5. The second inequality holds as an equality if and only if $\bar{\varphi}_{<j>} = 1$ for each $<j>$. That is, $\varphi \in \Phi^*(x) \Rightarrow \varphi_j = \hat{x}^o_j \quad \forall\, j \in C(x^o)$. Hence $\varphi \in \Phi^*(x^o)$. Thus

$$\text{(II.21)}\qquad \Phi^*(x) \subseteq \Phi^*(x^o).$$

Combine (II.21) with (II.17) and the theorem is proved. Q.E.D.

We can more fully describe Φ^* as a consequence of the next several results. We let:

$P^* = \{\pi \in E^m \mid c + \log \varphi = A^T\pi \text{ for some } \varphi \in \Phi\}$.

Lemma II.7: P* is convex.

Proof: Let $x \in M(F|H(A, b))$ have a maximal carrier $J = C(x)$. Then we may say that $\pi \in P^*$ if and only if π satisfies:

$$
\text{(II.22)} \quad \begin{cases} A^T{}_J\pi = c_J + \log \hat{x}_J \\ \\ \sum_{k\in\langle j\rangle} \exp(A_k^T\pi - c_k) \leq 1 \quad \text{for each } j \notin J. \end{cases}
$$

If we then let $\varphi_j = \exp(A_j^T\pi - c_j)$ for any π satisfying (II.22), the vector $\varphi \in \Phi^*$.

Since 'exp' is a convex function, it is clear that the constraints (II.22) describe a convex set. Q.E.D.

Lemma II.8: Suppose there exists $y \in H(A, b)$ such that $y > 0$, and let the matrix A have full rank m. Then P* is compact.

Proof: P*, the set of π satisfying (II.22), is surely closed. If it is not compact, it must be unbounded.

Since P* is convex, if it is to be unbounded, by [4], Lemma 3, there must exist a ray $\eta \neq 0$ such that for any $\pi \in P^*$, $\pi + t\eta \in P^*$ for every $t \geq 0$. Clearly (II.22) implies that η must satisfy:

$$
\text{(II.23)} \quad \begin{cases} A_j^T\eta = 0 \quad \text{if } j \in J \\ \\ A_j^T\eta \leq 0 \quad \text{if } j \notin J \end{cases}
$$

Let $x \in M(F|H)$ as in Lemma II.7, and let $y \in H(A, b)$ satisfy $y > 0$. If $\theta = y - x$, then clearly $\theta_j > 0$ if $j \notin J$. Further, since x and $y \in H(A, b)$, $A\theta = 0$. Thus, by (II.23),

$$\text{(II.24)} \qquad \theta^T A^T \eta = \sum_{j=1}^{n} \theta_j A_j^T \eta = \sum_{j \notin J} \theta_j A_j^T \eta = 0.$$

Again by (II.23), since $\theta_j > 0$ and $A_j^T \eta \leq 0$ if $j \notin J$, we must have $A_j^T \eta = 0$ if $j \notin J$. Hence,

$$\text{(II.25)} \qquad A^T \eta = 0.$$

Since A has full row rank m, (II.25) implies that

$$\text{(II.26)} \qquad \eta = 0.$$

Thus P* is bounded. Since it is closed as well, P* is compact. Q.E.D.

<u>Corollary II.9</u>: $Q^* = \{a \in E^n \mid \alpha = A^T \pi \text{ for some } \pi \in P^*\}$ is compact if there exists $y \in H(A, b)$ satisfying $y > 0$. That is, Q* is compact whatever the rank of A.

<u>Proof</u>: Let A have rank $r \leq m$, and let B be an $m \times m$ non-singular matrix such that $B^T A = \begin{pmatrix} \tilde{A} \\ 0 \end{pmatrix}$, where $\tilde{A}$ is an $r \times n$ matrix of rank r, and "0" denotes the $(m - r) \times n$ matrix consisting entirely of zeros. Let $\begin{pmatrix} \tilde{b} \\ 0 \end{pmatrix} = B^T b$. Clearly,

$$M(F|H(A, b)) = M(F|H(\tilde{A}, \tilde{b})).$$

Define $\tilde{P}^*$ to be the set of r-vectors η such that:

$$\tilde{A}_J^T\eta = c_J + \log \hat{x}_J$$

$$\sum_{k\in\langle j\rangle} \exp\,(\tilde{A}_k^T\eta - c_k) \leq 1 \qquad \forall\, j \notin J.$$

Clearly, $\eta \in \tilde{P}^*$ if and only if for some arbitrary $(m - r)$-vector γ, $B\begin{pmatrix}\eta\\ \gamma\end{pmatrix} = \pi \in P^*$.

Let:

$$\tilde{Q}^* = \{\alpha \in E^n \mid \alpha = \tilde{A}^T\eta \text{ for some } \eta \in \tilde{P}^*\}.$$

By Lemma II.8, $\tilde{P}^*$ is compact. As the range of a continuous (in fact linear) function whose domain is compact, surely $\tilde{Q}^*$ is compact. But it is easy to see that $Q^* = \tilde{Q}^*$.

Q.E.D.

__Theorem II.10__: Φ^* is compact if there exists $y \in H(A, b)$ satisfying $y > 0$.

__Proof__: $\varphi \in \Phi^*$ if and only if $\varphi_j = \exp(\alpha_j - c_j)$ for some $\alpha \in Q^*$. Since Φ^* is the range of a continuous function whose domain Q^* is compact, Φ^* must itself be compact.

Q.E.D.

It is not true that Φ^* is a convex set in general.

We defined Φ^* in such a way that for any compartment <j> which need not be empty at equilibrium (i.e., such that for some $x \in M(F|H)$, $\bar{x}_{\langle j\rangle} > 0$), $\bar{\xi}_{\langle j\rangle} = 1$ for every $\xi \in \Phi^*$, and further, any ξ^1, $\xi^2 \in \Phi^*$ agree in compartment <j>. The next result extends this idea slightly. It will prove important later.

Lemma II.11: Suppose for every $\xi \in \Phi^*$, $\bar{\xi}_{<j>} = 1$ for a particular $<j>$. Then for each $k \in <j>$, and every $\xi^1, \xi^2 \in \Phi^*$, $\xi_k^1 = \xi_k^2$.

Proof: Suppose $\xi^1, \xi^2 \in \Phi^*$, and $\xi_k^1 \neq \xi_k^2$ for some $k \in <j>$. Let $\pi^1, \pi^2 \in P^*$, be such that:

$$\xi^i = \exp(A^T\pi^i - c) \quad i = 1, 2.$$

Since P* is convex (Lemma II.7), $\eta = \dfrac{\pi^1 + \pi^2}{2}$ is an element of P*. Let:

$$\gamma = \exp(A^T\eta - c).$$

Clearly, then,

$$\bar{\gamma}_{<j>} = \sum_{k\in<j>} \left(\xi_k^1\xi_k^2\right)^{\frac{1}{2}}.$$

But for any a, b > 0, a $\neq$ b, it is well known that:

$$(ab)^{\frac{1}{2}} < \frac{a + b}{2}$$

Thus, since for some $k \in <j>$, $\xi_k^1 \neq \xi_2^k$, we have:

$$\bar{\gamma}_{<j>} = \sum_{k\in<j>} \left(\xi_k^1\xi_k^2\right)^{\frac{1}{2}} < \sum_{k\in<j>} \left(\frac{\xi_k^1 + \xi_k^2}{2}\right) = 1 \qquad \text{QED.}$$

III: Overcoming Degeneracy With Slacks

Although we now know how to recognize whether a composition x is a solution to problem (I.6) we still face several difficulties in trying to solve the problem. One of them is constructing the vector which satisfies the assumption made throughout the previous section, that there exists a vector $x \in H(A, b)$ such that $x > 0$. This is discussed in [7].

Other difficulties concern degeneracy. It may be, for example, that the solution set $M(F|H)$ of a particular problem contains more than one vector x. Or it may be that for some $x \in M(F|H)$, at least one phase is empty. To cope with this last difficulty, we have constructed the elaborate theory of Section II. This chapter develops from that theory a method that avoids both of these difficulties.

1. Slacks: General Form

We may insure in most cases that the problem we actually solve will have a unique, strictly positive solution by adding one extra variable to each compartment. These extra variables are called slacks. With them, the problem becomes:

$$\mathrm{Min}\left(\sum_j x_j\left(c_j + \log \frac{x_j}{\bar{x}_{<j>} + S_{<j>}}\right) + \sum_{<j>} S_{<j>} \log \frac{S_{<j>}}{\bar{x}_{<j>} + S_{<j>}}\right)$$

$$\text{(III.1.1)} \qquad \text{s.t.} \quad Ax = b$$

$$S_{<j>} = \varepsilon_{<j>} > 0$$

$$x \geq 0$$

The mole fractions are of course, changed by the addition of slacks. Thus in (III.1.1)

$$\text{(III.1.2)} \quad \hat{x}_j = \frac{x_j}{\bar{x}_{<j>} + S_{<j>}} \; ; \quad \hat{S}_{<j>} = \frac{S_{<j>}}{\bar{x}_{<j>} + S_{<j>}}$$

where $\bar{x}_{<j>}$ is as it was before.

Notice that this method of handling degeneracy does not require that the problem actually be expanded. Instead, we may treat the slacks implicitly, choosing a small positive $\varepsilon_{<k>}$ for each compartment $<k>$ and solving:

$$\mathrm{Min}\left(\sum_j x_j(c_j + \log \hat{x}_j) + \sum_{<j>} \varepsilon_{<j>} \log \hat{\varepsilon}_{<j>}\right)$$

$$\text{(III.1.3)} \qquad \text{s.t.} \quad Ax = b$$

$$x \geq 0 \; .$$

To compute $\hat{x}_j$ and $\hat{\varepsilon}_{<j>}$ in (III.1.3) we have substituted $\varepsilon_{<j>}$ for $S_{<j>}$ wherever the latter occured in (III.1.2). We define:

(III.1.4) $F_{\varepsilon}(x) = \sum_{j} x_j(c_j + \log \hat{x}_j) + \sum_{<j>} \varepsilon_{<j>} \log \hat{\varepsilon}_{<j>}$

where ε is the vector whose components are the $\varepsilon_{<j>}$.

Theorem III.1.1: Assume there exists $y \in H(A, b)$ satisfying $y > 0$. For each $\varepsilon > 0$, let $M(F_{\varepsilon}|H(A, b))$ be nonempty. Then it contains exactly one point $x(\varepsilon)$, and that point is a strictly positive vector.

Proof: Suppose $M(F_{\varepsilon}|H)$ is non-empty. Looking to (III.1.1) we see that by adding slacks to the problem, we have insured that the sum of variables, including the slacks, for each phase, must be strictly positive (in fact it can be no smaller than $\varepsilon_{<j>} > 0$). Thus the set J (of indices in non-vanishing compartments) must always include every index j.

But we know from Theorem II.4 that the solution must be strictly positive for each index in J. Hence every $x \in M(F_{\varepsilon}|H)$ is strictly positive.

Lemma 9.5, p. 370, of [5] states that if $x, y \in M(F_{\varepsilon}|H)$, then since $x, y > 0$:

$$\hat{x}_j = \hat{y}_j, \quad j = 1, 2, \ldots, n$$

where $\hat{x}_j$ and $\hat{y}_j$ are defined according to equation (III.1.2). In particular:

$$\frac{\varepsilon_{<j>}}{\bar{x}_{<j>} + \varepsilon_{<j>}} = \frac{\varepsilon_{<j>}}{\bar{y}_{<j>} + \varepsilon_{<j>}} .$$

Thus $\overline{x}_{<j>} = \overline{y}_{<j>}$. Simple algebra shows from this that $x = y$. QED.

Theorem III.1.2: Assume there exists $y \in H(A, b)$ such that $y > 0$. For each $\varepsilon > 0$, $M(F_\varepsilon|H)$ is non-empty if and only if $M(F|H)$ (the solution set of the problem unperturbed by slacks) is bounded and non-empty.

Proof: ($\Rightarrow$) Suppose $M(F|H)$ is empty or unbounded. Then [4], Theorems 2, 4 and 5, state that there must be a non-zero vector $\theta \in E^n$ satisfying:

$$\text{(III.1.5)} \qquad \begin{aligned} F(\theta) &\leq 0 \\ A\theta &= 0 \\ \theta &\geq 0, \quad \text{and } \theta \neq 0. \end{aligned}$$

Choose any $y \in H(A, b)$ such that $y > 0$. (We know from the previous Theorem III.1.1 that only such y are candidates for a solution to the perturbed problems.) Then:

$$F(y + t\theta) \leq F(y) + tF(\theta)$$

by the convexity and homogeneity of F. Thus

$$\text{(III.1.6)} \quad F_\theta'(y) = \lim_{t\to 0^+} \frac{F(y + t\theta) - F(y)}{t} \leq F(\theta) \leq 0 .$$

From equation (II.3) we may compute the directional derivative of F_ε at y in the direction θ to be:

$$\text{(III.1.7)} \quad \lim_{t\to 0^+} \frac{d}{dt} F_\varepsilon(y + t\theta) = F_\theta'(y) + \sum_{<j>} \overline{\theta}_{<j>} \log \frac{\overline{y}_{<j>}}{\overline{y}_{<j>} + \varepsilon_{<j>}} .$$

Since $\theta \geq 0$, each of the sums $\overline{\theta}_{<j>}$ is nonnegative. Because $\theta \neq 0$, for at least one $<j>$ we must have $\overline{\theta}_{<j>} > 0$. For every $<j>$, the fact that $\varepsilon_{<j>} > 0$ insures that:

$$\text{(III.1.8)} \qquad \log \frac{\overline{y}_{<j>}}{\overline{y}_{<j>} + \varepsilon_{<j>}} < \log 1 = 0.$$

Combining (VI.1.6–8) we find that:

$$\text{(III.1.9)} \qquad \lim_{t \to 0^+} \frac{d}{dt} F_\varepsilon(y + t\theta) < 0.$$

Thus by Theorem II.2, $y \notin M(F_\varepsilon|H)$. Since $y > 0$ was arbitrary, and since $y \in M(F_\varepsilon|H)$ implies $y > 0$, we know $M(F_\varepsilon|H)$ is empty.

($\Leftarrow$) If $M(F_\varepsilon|H)$ is empty, then by [4], Theorems 2, 4 and 5, there must exist a vector θ satisfying (III.1.5). This in turn implies, by [4] Theorems 4 and 5, that $M(F|H)$ is either unbounded or empty. Q.E.D.

We will assume throughout the remainder of this chapter that $M(F|H)$ is bounded and nonempty. In addition we will suppose that there exists $y \in H(A, b)$ satisfying $y > 0$. This will save us from including these assumptions in the hypotheses of each theorem.

Theorem III.1.3: For each vector $\varepsilon > 0$, let $M(F_\varepsilon|H(A, b)) = \{x(\varepsilon)\}$. Then $x(\varepsilon)$ and $\hat{x}(\varepsilon)$ are continuous functions of $\varepsilon > 0$.

Note: This statement is equivalent to saying that $x(\varepsilon)$ solves (III.1.1). By the previous two theorems, $x(\varepsilon)$ is a positive, single-valued vector function of the vector ε.

Proof: Since $x(\varepsilon) > 0$, $\hat{x}(\varepsilon)$ is well defined and continuous if $x(\varepsilon)$ is continuous. To see that $x(\varepsilon)$ is continuous, see [8], Cor. I.2.4, p. 528. QED.

It is our purpose in this section to show that the continuity of $x(\varepsilon)$ and $\hat{x}(\varepsilon)$ extend in some sense to $\varepsilon = 0$, which characterizes the original problem, (I.6). That is, we wish to show that if each component of ε is chosen sufficiently small, then the solution $x(\varepsilon)$ will be as close as desired to some solution of the original problem, and $\hat{x}(\varepsilon)$ will approximate a vector of virtual mole fractions.

Lemma III.1.4: Let $\{\varepsilon^k\}$ be a sequence satisfying $\varepsilon^k > 0 \; \forall k$ and $\varepsilon^k \to 0$. Then there exists an infinite subsequence S of (1, 2, ...) such that $x^o = \lim_{k \in S} x(\varepsilon^k)$ exists, and for each such subsequence,

(III.1.10) $$x^o \in M(F|H(A, b)).$$

Proof: [8], Corollary II.3.1, p. 545, and Theorem I.2.2, p. 526; and Theorems III.1.1–2 above. Q.E.D.

Theorem III.1.5: Let $\{\varepsilon^k\}$ be as in Lemma III.1.4. Then there exists a subsequence S of (1, 2, ...) such that $\xi = \lim_{k \in S} \hat{x}(\varepsilon^k)$ exists, and for each such ξ we have that:

(III.1.11) $$\xi \in \xi^*.$$

Proof: Since for every j and k, $0 < \hat{x}_j(\varepsilon^k) < 1$, we can find a subsequence S of (1, 2, ...) so that $\xi = \lim_{k \in S} \hat{x}(\varepsilon^k)$ exists.

By Lemma III.1.4, we may find a subsequence S' of S such that $x^o = \lim_{k \in S'} x(\varepsilon^k)$ exists, and $x^o \in M(F|H)$.

Since $x(\varepsilon^k) \in M(F_\varepsilon|H)$, and since $x(\varepsilon^k) > 0$ for each k (making every reaction vector admissible at $x(\varepsilon^k)$), we know that for each θ satisfying $A\theta = 0$, we must have $\theta \cdot (c + \log \hat{x}(\varepsilon^k)) = 0$. Taking the limit of this expression as $k \in S'$ becomes infinite, we find:

$$\text{(III.1.12)} \qquad \theta \cdot (c + \log \xi) = 0 \quad \forall \theta \ni A\theta = 0.$$

Clearly, for each phase <j>,

$$\text{(III.1.13)} \qquad \xi_{<j>} = \lim_{k \in S'} \left(\sum_{\ell \in <j>} \hat{x}_\ell(\varepsilon^k) \right) \le 1.$$

It is easy to show that for each j such that $\hat{x}_j^o$ is defined,

$$\text{(III.1.14)} \qquad \xi_j = \hat{x}_j^o$$

and that for every j,

$$\text{(III.1.15)} \qquad \xi_j > 0.$$

By (III.1.12–15), and Theorem II.6,

$$\xi \in \Phi^*.$$

Q.E.D.

2. Slacks: Special Form

The most natural sequences $\{\varepsilon^k\}$ one may consider are those which take the form,

$$\varepsilon^k = t_k \sigma \tag{III.2.1}$$

where σ is a constant vector with one strictly positive element corresponding to each compartment and $\{t_k\}$ is a sequence of positive real numbers whose limit is zero. In this section we will explore the properties of the sequence of solutions $\{x(\varepsilon^k)\}$ to problem (III.1.3), where ε^k takes the form of (III.2.1).

We shall change our notation somewhat. Instead of writing $F_\varepsilon(x)$, we will write $F(x;\ t)$, where:

$$F(x;\ t) = \left[\sum_j x_j\left(c_j + \log \frac{x_j}{\bar{x}_{<j>} + t\sigma_{<j>}}\right) + \sum_{<j>} t\sigma_{<j>} \log \frac{t\sigma_{<j>}}{\bar{x}_{<j>} + t\sigma_{<j>}}\right] . \tag{III.2.2}$$

The sums $\bar{x}_{<j>}$ do not include the slacks, $t\sigma_{<j>}$. Also, in writing $F(x;\ t)$ we understand that the vector σ will be constant, and so do not mention it. In the same way, we will replace $x(t\sigma)$ by $x(t)$, leaving the constant vector σ out.

We shall show that $\hat{x}(t)$ approaches a limit as $t \to 0$, and we shall identify the limit. We shall attempt to do the same for $x(t)$, but, as the reader will see, we fall somewhat short of complete success.

Take $\hat{x}(t)$ first. Define the sets:

$$J = \{j | \bar{\xi}_{<j>} = 1 \quad \forall \xi \in \Phi^*\}$$

$$I = \{j \notin J\}.$$

In addition it will be convenient to define the related sets:

$$J^* = \{<j> | j \in J\} = \{<j> | \bar{\xi}_{<j>} = 1 \quad \forall \xi \in \Phi^*\}$$

$$I^* = \{<j> | j \in I\} = \{<j> \notin J^*\}$$

We know that for $j \in J$, $\hat{x}_j(t)$ must converge as $t \to 0$, since it is bounded, since by Theorem III.1.5 every limit point of $\hat{x}(t)$ must be an element of Φ^*, and since by Lemma II.11, there is for $j \in J$ only one possible value for ξ_j if $\xi \in \Phi^*$.

For each j, define a function of π as follows:

$$\xi_j(\pi) = \exp(A_j^T\pi - c_j). \qquad \text{(III.2.3)}$$

We know from Theorem II.4, and definitions (II.5b) and (II.15) that if $\pi(t)$ is the vector of Lagrange multipliers corresponding to the solution $x(t)$, then $\hat{x}_j(t) = \xi_j(\pi(t))$. Substituting for $\hat{x}_j(t)$ from equation (III.1.2), we may solve for the quantities $x_j(t)$, $1 \leq j \leq \eta$ in terms of the quantities $\xi_j(\pi(t))$, $1 \leq j \leq n$ and the slacks $t\sigma_{<j>}$. The result is just:

$$x_j(t) = \frac{t\sigma_{<j>}\xi_j(\pi(t))}{1 - \bar{\xi}_{<j>}(\pi(t))}. \qquad \text{(III.2.4)}$$

Suppose that $x^o \in M(F|H)$. Then we know that:

$$\text{(III.2.5)} \qquad \sum_{j\in I} A_j x_j(t) = -\sum_{j\in J} A_j(x_j(t) - x_j^o).$$

Substituting (III.2.4) into (III.2.5) for $j \in I$ we find that:

$$\text{(III.2.6)} \qquad \sum_{j\in I} \frac{t\sigma_{<j>} A_j \xi_j(\pi(t))}{1 - \overline{\xi}_{<j>}(\pi(t))} = -\sum_{j\in J} A_j(x_j(t) - x_j^o).$$

A simple computation from (III.2.3) shows that if:

$$g_t(\pi) = -\sum_{<j>\in I^*} t\sigma_{<j>} \log(1 - \overline{\xi}_{<j>}(\pi))$$

then:

$$\text{(III.2.7)} \qquad \sum_{j\in I} \frac{t\sigma_{<j>} A_j \xi_j(\pi)}{(1 - \overline{\xi}_{<j>}(\pi))} = \nabla g_t(\pi).$$

By (III.2.7), equation (III.2.6) is the optimality condition for the problem:

$$\text{(III.2.8)} \qquad \begin{array}{l} \text{Min } g_t(\pi) \\ \text{s. t.} \quad A_J^T \pi = c_J + \log \hat{x}_J(t) \end{array}.$$

That is, if we knew for any fixed t the values of $\hat{x}_J(t)$, then $\pi(t)$ would be a solution of (III.2.8).

<u>Lemma III.2.1</u>: If the matrix A has full rank m, then (III.2.8) possesses a unique solution $\pi(t)$.

<u>Proof</u>: We know that (III.2.8) is feasible. That is $\pi(t)$ satisfies $A_J^T\pi(t) = c_J + \log \hat{x}_J(t)$.

For $t > 0$, we may compute the matrix of second partial derivatives of g. This becomes,

$$\text{(III.2.9)} \quad \nabla^2 g_t(\pi) = \sum_{j\in I} \frac{t\sigma_{<j>}A_j\xi_jA_j^T}{(1-\bar{\xi}_{<j>})} + \sum_{<j>\in I^*} \frac{t\sigma_{<j>}\hat{\beta}_{<j>}\hat{\beta}_{<j>}^T}{(1-\bar{\xi}_{<j>})},$$

where $\hat{\beta}_{<j>} = \sum_{k\in<j>} A_k\xi_k$. Clearly $\nabla^2 g_t(\pi)$ is a positive semidefinite matrix for all π such that $\bar{\xi}_{<j>}(\pi) < 1$, $j \in I$, so that $g(\pi)$ is convex on P^*.

Further, for any $v \in E^m$,

$$\text{(III.2.10)} \qquad v^T(\nabla^2 g_t(\pi))v = 0 \Leftrightarrow A_I^T v = 0.$$

To see that (III.2.10) is true, let Y be a diagonal matrix with as many columns as there are indices in I. The $jj^{\underline{th}}$ component of Y shall be $y_j = \dfrac{t\sigma_{<j>}\xi_j}{1-\bar{\xi}_{<j>}} > 0$. Then the first term of (III.2.9) becomes $A_I Y A_I^T$; by elementary linear algebra one may show that $v^T A_I Y A_I^T v = 0$ if and only if $A_I^T v = 0$. A similar comment applies to the second term of (III.2.9).

If there are two solutions π^1 and π^2 to (III.2.8) they must differ by such a v. Further, since each solution satisfies the constraints, $\pi^1 - \pi^2 = v$ must also satisfy $A_J v = 0$. Hence $Av = 0$. Since A has full rank m, $v = 0$, so the solution $\pi(t)$ of (III.2.8) is unique. Q.E.D.

Next we wish to establish that $\hat{x}(t)$ must approach a limit as $t \to 0$. We will again assume that A has full rank m.

<u>Theorem III.2.2</u>: $\xi = \lim_{t\to 0} \hat{x}(t)$ exists, and $\xi = \xi(\pi^*)$, where π^* is the unique solution to:

$$\text{(III.2.11)} \quad \text{Min} \left[-\sum_{<j>\in I^*} \sigma_{<j>} \log (1 - \xi_{<j>}(\pi)) \right]$$

$$\text{s.t.} \quad A_J^T \pi = c_J + \log \xi_J .$$

($\xi_J = \lim_{t\to 0} \hat{x}_J(t)$, which we know exists.)
In particular $\xi_{<j>} < 1$ for each $<j> \in I^*$.

<u>Proof</u>: For each $t > 0$, $\pi(t)$ must satisfy:

$$\text{(III.2.12)} \quad \text{Min} \left[-\sum_{<j>\in I^*} \sigma_{<j>} \log (1 - \xi_{<j>}(\pi)) \right]$$

$$\text{s.t.} \quad A_J^T \pi = c_J + \log \hat{x}_J(t).$$

This is just (III.2.8) where we have divided the objective function $g_t(\pi)$ by t.

We know that $\hat{x}_j(t)$ is continuous for $j \in J$, and is bounded away from zero. Thus the right-hand side ($c_J + \log \hat{x}_J(t)$) of the constraint set of (III.2.12) is continuous at $t = 0$.

Furthermore, at $t = 0$, problem (III.2.12) has a unique solution by Lemma III.2.1. Thus by [8], Corollary II.3.1 and Theorem I.3.2, we know that the solution $\pi(t)$ to (III.2.12) is continuous at $t = 0$; hence $\hat{x}(t)$ is continuous at zero, and $\xi = \lim_{t\to 0} \hat{x}(t)$ must satisfy (III.2.11). Q.E.D.

Next we wish to work on $x(t)$ itself. As we stated earlier, we have been unable to prove that $x(t)$ approaches a limit as $t \to 0$. For the reasons that follow, we conjecture that $x(t)$ does have a limit.

Let $\xi \in \Phi^*$ be the limit of $\hat{x}(t)$ as described in Theorem III.2.2. By [5], Lemma 9.7, p. 370, we know there exists $y^o \in M(F|H)$ such that for every compartment $<j>$, $\bar{y}^o_{<j>} = 0$ implies that $\bar{x}_{<j>} = 0$ for each $x \in M(F|H)$. We define the index sets:

$$I = \{j|\bar{\xi}_{<j>} < 1\} \quad ; \quad I^* = \{<j>|j \in I\}$$
$$J = \{j|\bar{y}^o_{<j>} > 0\} \quad ; \quad J^* = \{<j>|j \in J\}$$
$$K = \{j \notin J|\bar{\xi}_{<j>} = 1\} \quad ; \quad K^* = \{<j>|j \in K\} .$$

Lemma III.2.3: Let $M(F|H)$ be bounded and nonempty, and suppose there exists $y \in H(A, b)$ such that $y > 0$. Then there exists a unique solution x^* to the problem:

$$\text{(III.2.13)} \quad \text{Min } g(x) = \text{Min}\left(-\sum_{<j>\in J^*} \sigma_{<j>} \log \bar{x}_{<j>}\right)$$

$$\text{s.t.} \quad x \in M(F|H) .$$

Further, for each $j \in J$, $x^*_j > 0$.

Proof: From [5], Theorem 9.5, p. 370, we can write $M(F|H(A, b))$ as the set of solutions to a system of linear equations together with nonnegativity constraints. Let $y^o \in M(F|H)$ satisfy $y^o_j > 0$ for each $j \in J$, and define:

$$\text{(III.2.14)} \quad \hat{\beta}_{<j>} = \sum_{k\in<j>} A_k\hat{y}^o_k \quad j \in J.$$

Then $x \in M(F|H)$ if and only if:

$$(\text{III.2.15})\begin{cases}(a) & \hat{x}_j = \hat{y}_j^o \text{ for every } j \in J \text{ such that } \overline{x}_{<j>} > 0, \\ (b) & x_j = 0 \text{ for } j \notin J \\ (c) & \sum_{<j>\in J^*} \hat{\beta}_{<j>}\overline{x}_{<j>} = b,\ \overline{x}_{<j>} \geq 0.\end{cases}$$

If we find any solution $\overline{x}$ to (III.2.15c) we may reconstruct a unique element x of $M(F|H(A, b))$ by using (III.2.15a–b). Further, that element x will satisfy $x_j > 0$ for each $j \in J$ if and only if $\overline{x}_{<j>} > 0$ for every $j \in J$.

Thus (III.2.13) is equivalent to solving:

$$(\text{III.2.16})\quad \text{Min } g(x) = \text{Min}\left(-\sum_{<j>\in J^*} \sigma_{<j>} \log \overline{x}_{<j>}\right)$$

$$\text{s.t.} \quad \sum_{<j>\in J^*} \hat{\beta}_{<j>}\overline{x}_{<j>} = b$$

$$\overline{x}_{<j>} \geq \omega .$$

It is easy to see that g(x), as a function of the $\overline{x}$'s, is strictly convex. Since the constraint set is bounded (i.e., $M(F|H)$ is bounded), (III.2.16) has a unique solution. Since there exists a positive feasible solution, and since g(x) is infinite if some $\overline{x}_{<j>} = 0$, $j \in J$, it is clear that the solution x^* to (III.2.16) is positive on J. Q.E.D.

We conjecture that x(t) has a limit as $t \to 0$, and that $\lim_{t\to 0} x(t) = x^*$.

By definition, $x(t)$ is the unique point in $M(F(\cdot, t)|H)$. Thus, $x(t)$ is also a solution (though not necessarily the unique solution) to:

(III.2.17)

$$\text{Min } G(y, t) = \text{Min} \sum_{I \cup K} y_j\left(c_j + \log \frac{y_j}{\bar{y}_{<j>}} + \log \frac{\bar{x}_{<j>}(t)}{\bar{x}_{<j>}(t) + t\sigma_{<j>}}\right)$$

$$+ \sum_J y_j\left(c_j + \log \frac{y_j}{\bar{y}_{<j>} + t\sigma_{<j>}}\right) - \sum_{<j>\in J^*} t\sigma_{<j>} \log(\bar{y}_{<j>} + t\sigma_{<j>})$$

$$\text{s.t.} \quad y \in H(A, b).$$

It is easy to see that $G(y, t)$ is convex for fixed t, though it is not necessarily strictly convex; and surely $x(t)$ satisfies the condition that:

$$\frac{\partial G(x(t), t)}{\partial y_j} = c_j + \log \hat{x}_j(t) = A_j^T\pi(t).$$

We separate $G(y, t)$ into two parts. Let:

(III.2.18a) $$g(y, t, \beta) = \sum y_j\left(c_j + \log \frac{y_j}{\bar{y}_{<j>}}\right) + \beta\sum_{<j>\in I^*} \bar{y}_{<j>} \log \frac{\bar{x}_{<j>}}{\bar{x}_{<j>} + t\sigma_{<j>}}$$

(III.2.18b) $$h(y, t, \beta) = \frac{1}{t}[G(y, t) - g(y, t, \beta)].$$

If we then define the set:

(III.2.19) $$S_\beta(t) = \{y \in H | g(y, t, \beta) \leq g(x(t), t, \beta)\}$$

then it is obvious that for any $t > 0$,

(III.2.20) $y \in S_\beta(t) \Rightarrow h(y, t, \beta) \geq h(x(t), t, \beta)$.

Equivalently we may write:

(III.2.21) $x(t) \in M(h(\cdot, t, \beta)|S_\beta(t))$.

Lemma III.2.4: Let $M(F(\cdot, 0)|H)$ be bounded and nonempty. Then for any $0 < \beta < 1$, $M(F(\cdot, 0)|H) \subset S_\beta(t)$, for all $t > 0$ sufficiently small.

Proof: Note that $g(y, t, \beta)$ is convex in y for fixed t and β. Let $x^o \in M(F(\cdot, 0)|H)$.

Notice that $g(y, t, \beta)$ is a Gibbs function with each c_j, for $j \in I$, modified to:

$$c_j' = c_j + \beta \log \frac{\bar{x}_{<j>}(t)}{\bar{x}_{<j>}(t) + w_{<j>}} = c_j + \beta \log \xi_{<j>}(t), \quad j \in I.$$

Let $\xi = \lim_{t \to 0} \hat{x}(t)$, as in Theorem III.2.2. We know that $\xi \in \mathfrak{F}^*$. If we replace c_j by d_j for every $j \in I$, where:

$$d_j = c_j + \log k_{<j>} \quad j \in I$$

and $\log k_{<j>} \geq \log \xi_{<j>}$ then clearly ξ' defined by $\xi_j' = \frac{\xi_j}{k_{<j>}}$ is an element of the new $\mathfrak{F}^*$, so that x^o is a solution to the perturbed problem.

But for given $\beta < 1$, we can always pick $t_\beta > 0$ sufficiently small so that for $0 \leq t \leq t_\beta$,

$$\beta \log \frac{\bar{x}_{<j>}(t)}{\bar{x}_{<j>}(t) + t\sigma_{<j>}} > \log \xi_{<j>} .$$

Thus $x^o \in S_\beta(t)$ for $0 \leq t \leq t_\beta$. Since $g(x, t\ \beta)$ is constant on $M(F(\cdot, 0)|H)$,

$$M(F(\cdot, 0)|H) \subset S_\beta(t) \quad 0 \leq t \leq t_\beta .$$

Q.E.D.

The next item we must study is the function $h(y, t, \beta)$. This we deal with in two lemmas.

<u>Lemma III.2.5</u>: Let $x^o \in M(F(\cdot, 0)|H)$ be fixed. Then

$$\lim_{t \to 0} h(x^o, t, \beta) = \begin{cases} -\sum_{<j> \in J^*} \sigma_{<j>} \log \bar{x}^o_{<j>} - \sum_{<j> \in J^*} \sigma_{<j>} & \text{if } C(x^o) = J \\ \infty & \text{if } C(x^o) \subsetneq J. \end{cases}$$

<u>Proof</u>: Since $x^o \in M(F(\cdot, 0)|H)$, $x^o_j = 0$ if $j \in I \cup K$. Thus from (III.2.17) and (III.2.18b),

$$h(x^o, t, \beta) = \frac{1}{t} \sum_{<j> \in J^*} \bar{x}^o_{<j>} \log \frac{\bar{x}^o_{<j>}}{\bar{x}^o_{<j>} + t\sigma_{<j>}}$$
$$- \sum_{<j> \in J^*} \sigma_{<j>} \log(\bar{x}^o_{<j>} + t\sigma_{<j>}).$$

Suppose for some $j \in J$, $\bar{x}^o_{<j>} = 0$. Then:

$$\bar{x}^o_{<j>} \log \frac{\bar{x}^o_{<j>}}{\bar{x}^o_{<j>} + t\sigma_{<j>}} = 0 \text{ by definition, for all } t > 0$$

and: $-\sigma_{<j>} \log\left(\bar{x}^o_{<j>} + t\sigma_{<j>}\right) = -\sigma_{<j>} \log t\sigma_{<j>} \to \infty$ as $t \to 0$.

On the other hand, if $\bar{x}^o_{<j>} > 0$, we see that:

$$\frac{1}{t}\left[\bar{x}^o_{<j>} \log \frac{\bar{x}^o_{<j>}}{\bar{x}^o_{<j>} + t\sigma_{<j>}}\right] = \frac{\bar{x}^o_{<j>}}{t} \sum_{k\epsilon 1}^{\infty} \frac{1}{k}\left(\frac{t\sigma_{<j>}}{\bar{x}^o_{<j>}}\right)^k (-1)^k \to -\sigma_{<j>}.$$

Also,

$$-\sigma_{<j>} \log (\bar{x}^o_{<j>} + t\sigma_{<j>}) \to -\sigma_{<j>} \log \bar{x}^o_{<j>}.$$

Thus the lemma is proved. QED.

Lemma III.2.6: Let $\{t_n\}$ be a sequence satisfying $t_n > 0$ for every n, $t_n \to 0$ and $x(t_n) \to y^o \in M(F|H)$ as $n \to \infty$.

Let $h_n = h(x(t_n), t_n, \beta)$. Then if the carrier $C(y^o) \subsetneq J$, $\lim_{n\to\infty} h_n = \infty$. Otherwise (i.e., if $C(y^o) = J$)

$$\lim_{n\to\infty} h_n = (1-\beta) \sum_{<j>\epsilon I^*} \frac{\sigma_{<j>}\xi_{<j>} \log \xi_{<j>}}{1-\xi_{<j>}} - \sum_{<j>\epsilon K^* \cup J^*} \sigma_{<j>}$$

$$- \sum_{<j>\epsilon J^*} \sigma_{<j>} \log \bar{y}^o_{<j>}$$

where $\xi = \lim_{n\to\infty} \hat{x}(t_n)$.

Proof: From equation (III.2.4), if $j \in I$,

$$\text{(III.2.22)} \quad \lim_{n\to\infty} \frac{1}{t}\bar{x}_{<j>}(t) \log \frac{\bar{x}_{<j>}(t)}{\bar{x}_{<j>}(t) + t\sigma_{<j>}} = \frac{\sigma_{<j>}\xi_{<j>} \log \xi_{<j>}}{1-\xi_{<j>}}$$

If $j \in J \cup K$, we see that:

$$\log \frac{\overline{x}_{<j>}}{\overline{x}_{<j>} + t\sigma_{<j>}} \approx \frac{t\sigma_{<j>}}{\overline{x}_{<j>} + t\sigma_{<j>}} + 0\left(\left(\frac{t\sigma_{<j>}}{\overline{x}_{<j>} + t\sigma_{<j>}}\right)^2\right).$$

Multiplying by $\frac{\overline{x}_{<j>}(t_n)}{t_n}$ and taking the limit as $n \to \infty$, clearly the error term vanishes. We are left with:

$$\text{(III.2.23)} \quad \lim_{n\to\infty} \frac{\overline{x}_{<j>}(t_n)}{t_n} \log \frac{\overline{x}_{<j>}(t_n)}{\overline{x}_{<j>}(t_n) + t_n\sigma_{<j>}}$$

$$= -\sigma_{<j>} \quad (j \in J \cup K).$$

The remaining term is easy.

$$\text{(III.2.24)} \quad -\lim_{n\to\infty} \sum_{<j>\in J^*} \sigma_{<j>} \log (\overline{x}_{<j>}(t_n) + t_n\sigma_{<j>})$$

$$= \begin{cases} -\sum\limits_{<j>\in J^*} \sigma_{<j>} \log \overline{y}^o_{<j>} & \text{if } C(y^o) = J \\ \infty & \text{if } C(y^0) \subsetneq J. \end{cases}$$

Putting Equations (III.2.22–24) and (III.2.18b) together, yield the result we wish. QED.

These last three lemmas enable us to prove the following theorem.

Theorem III.2.7: Let $M(F(\cdot, 0)|H)$ be bounded. Let $\{t_n\}$ be such that $t_n > 0$ for each n, $t_n \to 0$ as $n \to \infty$, and $x(t_n)$

$\to y^o \in M(F(\cdot, 0)|H)$ as $n \to \infty$. Then:

$$0 \le -\sum_{\langle j\rangle \in J^*} \sigma_{\langle j\rangle} \log \frac{\overline{y}^o_{\langle j\rangle}}{\overline{x}^*_{\langle j\rangle}} \le \sum_{\langle j\rangle \in K^*} \sigma_{\langle j\rangle} .$$

Proof: For sufficiently large n (i.e., sufficiently small $t > 0$), Lemma III.2.4 tells us that

$$x^* \in S_\beta(t)$$

since $x^* \in M(F(\cdot, 0)|H)$. Thus for n sufficiently large, we have by (III.2.20) that:

$$\text{(III.2.25)} \quad h(x^*, t_n, \beta) \ge h(x(t_n), t_n, \beta).$$

Thus, taking limits as $n \to \infty$ of both sides of (III.2.25) we find that Lemmas VI.2.5–6 imply:

$$\text{(III.2.26)} \quad -\sum_{\langle j\rangle \in J^*} \sigma_{\langle j\rangle} \log \overline{x}^*_{\langle j\rangle} \ge (1-\beta) \sum_{\langle j\rangle \in I^*} \frac{\sigma_{\langle j\rangle} \overline{\xi}_{\langle j\rangle} \log \overline{\xi}_{\langle j\rangle}}{1 - \overline{\xi}_{\langle j\rangle}}$$

$$- \sum_{\langle j\rangle \in K^*} \sigma_{\langle j\rangle} - \sum_{\langle j\rangle \in J^*} \sigma_{\langle j\rangle} \log \overline{y}^o_{\langle j\rangle} .$$

Clearly, since the left-hand side of (III.2.26) is finite, the right-hand side cannot be ∞; hence, $C(y^o) = J$, by Lemma III.2.6.

Further, by Lemma III.2.4, Equation (III.2.26) is true for every $\beta < 1$. Thus letting $\varepsilon = (1 - \beta) > 0$ be as small as we wish, we see that, as the theorem says, (III.2.27) $0 \leq -\sum_{<j>\in J^*} \sigma_{<j>} \log \frac{\bar{y}^o_{<j>}}{\bar{x}^*_{<j>}} \leq \sum_{<j>\in K^*} \sigma_{<j>}$.

The left-hand inequality is a consequence of Lemma III.2.3, since $y^o \in M(F(\cdot, 0)|H)$. QED.

The important corollaries of Theorem III.2.7 are as follows.

Corollary III.2.8: If $y^o \in M(F(\cdot, 0)|H)$ is a limit point of $x(t)$ as $t \to 0$, then $C(y^o) = J$.

Proof: Immediate.

Corollary III.2.9: If K is empty (i.e., if for every $j \notin J$, $\bar{\xi}_{<j>} < 1$), then $x(t)$ has a limit x^* as $t \to 0$.

Proof: If K is empty then the upper limit on

$$-\sum_{<j>\in J^*} \sigma_{<j>} \log \frac{\bar{y}^o_{<j>}}{\bar{x}^*_{<j>}}$$

is zero. Thus:

$$-\sum_{<j>\in J^*} \sigma_{<j>} \log \bar{y}^o_{<j>} = -\sum_{<j>\in J^*} \sigma_{<j>} \log \bar{x}^*_{<j>} .$$

By Lemma III.2.3, since x^* uniquely solves (III.2.13) we must have $y^o = x^*$, for each limit point y^o of $x(t)$. QED.

We conjecture that regardless of whether K is empty, $x(t)$ has a limit, and $\lim_{t\to 0} x(t) = x^*$. The reasons supporting this conjecture are three. First, every example we have tried leads us to the limit x^*. Second, we have the following result.

Lemma III.2.10: Let every compartment $<j>$ satisfying $j \in J$ be identical to every other. That is, if j_1 and j_2 are any two indices in J, with $<j_1> \neq <j_2>$, then for every $k_1 \in <j_1>$, there is a $k_2 \in <j_2>$ such that columns k_1 and k_2 of the matrix A are identical, and $c_{k_1} = c_{k_2}$. In this case $x(t) \to x^*$.

Proof: Clearly,

$$c_{k_1} + \log \hat{x}_{k_1}(t) = A_{k_1}^T \pi(t) = c_{k_2} + \log \hat{x}_{k_2}(t) \quad \text{(III.2.28)}$$

at the equilibrium solution, since $A_{k_1} = A_{k_2}$. Thus:

$$\hat{x}_{k_1}(t) = \hat{x}_{k_2}(t) . \quad \text{(III.2.29)}$$

Summing over all $k_1 \in <j_1>$ and $k_2 \in <j_2>$, and performing some simple manipulations, we find that there exists a number $\lambda(t)$ for each $t > 0$ such that:

$$-\frac{\sigma_{<j>}}{\bar{x}_{<j>}(t) + t\sigma_{<j>}} = \lambda(t) \qquad \forall <j> \in J^*. \quad \text{(III.2.30)}$$

If we let:

$$(\text{III.2.31})\quad \begin{cases} \hat{\beta}_{<j>}(t) = \sum_{k\in<j>} A_k\hat{x}_k(t)\,, & \forall <j> \in J^* . \\ b(t) = b - \sum_{k\in I\cup K} A_k x_k(t)\,. \end{cases}$$

we notice that by (III.2.29), each $\hat{\beta}_{<j>}(t)$, for $<j> \in J^*$, is identical to every other, and that since:

$$(\text{III.2.32})\quad \sum_{<j>\in J^*} \hat{\beta}_{<j>}(t)(\overline{x}_{<j>}(t) + t\sigma_{<j>}) = b(t)$$

we see that $b(t)$ must be a multiple of $\hat{\beta}_{<j>}(t)$. Let $b(t) = k(t)\hat{\beta}_{<j>}(t)$. Then Equation (III.2.32) is equivalent to:

$$(\text{III.2.33})\quad \sum_{<j>\in J^*} (\overline{x}_{<j>}(t) + t\sigma_{<j>}) = k(t).$$

Equations (III.2.30) say that $x(t)$ solves the problem:

$$\text{Min}\left[-\sum_{<j>\in J^*} \sigma_{<j>} \log(\overline{x}_{<j>} + t\sigma_{<j>})\right]$$

$$(\text{III.2.34})\quad \text{s.t.}\quad \sum_{<j>\in J^*} (\overline{x}_{<j>} + t\sigma_{<j>}) = k(t)$$

$$x \in H(A, b)\,.$$

Since (III.2.32) and (III.2.33) are equivalent, problem (III.2.34) is the same as minimizing the same function subject to $x \in H(A, b)$ and x satisfying (III.2.32) in place of (III.2.33).

But $\hat{x}_j(t)$ is continuous at $t = 0$, so that $\hat{\beta}_{<j>}(t)$ is continuous at $t = 0$, and $x_{I \cup K}(t)$ tend to zero at $t = 0$, so that $b(t)$ is continuous and tends to b at $t = 0$. Thus in the limit as $t \to 0$, problem (III.2.34) is equivalent to the problem that defines x^*, i.e., problem (III.2.16). Thus by [8], Corollary II.3.1 and Theorem I.3.2,

$$\lim_{t \to 0} x(t) = x^*.$$

QED.

The third bit of evidence supporting the conjecture is that in two senses, a problem with a non-empty set of indices K is the limit of a sequence of problems with K empty.

<u>Lemma III.2.11</u>: Let

$$\hat{\beta}_K = \sum_{j \in K} A_j \xi_j$$

where $\xi \in \Phi^*$. (By Lemma II.11, every $\xi \in \Phi^*$ is the same for indices $j \in K$.) Let:

$$H_\delta = \{x | Ax = b + \delta \hat{\beta}_K, \ x \geq 0\}.$$

Then

$$\lim_{\delta \to 0^+} M(F|H_\delta) = M(F|H).$$

<u>Note 1</u>: The limit of a set is as defined in [8].

<u>Note 2</u>: The effect of this perturbation is to move each index originally in K to J.

Proof: Notice that this perturbation allows us to construct a solution x to the problem from any solution $x^o \in M(F|H(A, b))$ by

$$x_j = \begin{cases} x_j^o \text{ if } j \in J \\ 0 \text{ if } j \in I \\ \delta\xi_j \text{ if } j \in K \end{cases} ;$$

By [5], Theorem 9.5, p. 370 we know that any element of $M(F|H_\delta)$ must be quasidependent on this solution x. That is, we have for the perturbed problem the same δ^* as for the original.

But we argued in Lemma III.2.3 that we could write a set of linear constraints describing $M(F|H(A, b))$; and we may do the same for $M(F|H_\delta)$. Thus $x \in M(F|H_\delta)$ if and only if the sums $\bar{x}_{<j>}$ (for $j \in J \cup K$) satisfy,

$$\text{(III.2.35)} \qquad \sum_{<j>\in J^*\cup K^*} \hat{\beta}_{<j>}\bar{x}_{<j>} = b + \delta\hat{\beta}_K$$

$$\bar{x}_{<j>} \geq 0 \qquad \forall <j>$$

where

$$\hat{\beta}_{<j>} = \sum_{k\in<j>} A_k\xi_k \ .$$

But by [8], Corollary II.3.1, the limit of the set of x satisfying (III.2.35) is exactly the set satisfying:

$$\text{(III.2.36)} \qquad \sum_{<j>\in J^*\cup K^*} \hat{\beta}_{<j>}\overline{x}_{<j>} = b$$

$$\overline{x}_{<j>} \geq 0 \quad \forall <j> .$$

However, (III.2.36) implies that $\overline{x}_{<j>} = 0$ whenever $j \in K$; for if not, then there would be an $x \in M(F|H(A, b))$ such that $x_j > 0$ for $j \in K$, contradicting the definition of K. Thus (III.2.36) describes $M(F|H(A, b))$, and:

$$\lim M(F|H_\delta) = M(F|H(A, b))$$

QED.

It would be easy but pointless to prove that if x^*_δ solved:

$$\text{Min} \left(-\sum_{<j>\in J^*\cup K^*} \sigma_{<j>} \log \overline{x}_{<j>} \right)$$

$$\text{s.t.} \qquad \sum_{<j>\in J^*\cup K^*} \hat{\beta}_{<j>}\overline{x}_{<j>} = b + \delta\hat{\beta}_K$$

$$\overline{x}_{<j>} \geq 0 \quad \forall\, j \in J \cup K ,$$

then $\lim_{\delta\to 0^+} x^*_\delta = x^*$, where x^* is defined in Lemma III.2.3.

There is a second way we can perturb the problem so that it satisfies the condition that K be empty. This is by changing the c values.

<u>Lemma III.2.12</u>: Define new values for the c_j's as follows:

$$\bar{c}_j = \begin{cases} c_j & \text{if } j \in I \cup J \\ c_j + \varepsilon & \text{if } j \in K \end{cases}$$

for some small $\varepsilon > 0$.

For the new problem let the objective be:

$$\text{(III.2.37)} \qquad \bar{F}(x) = \Sigma\, x_j(\bar{c}_j + \log \hat{x}_j)$$
$$= F(x) + \varepsilon \sum_{j \in K} x_j \ .$$

Then:

(III.2.38) $M(\bar{F}|H) = M(F|H)$, for each $\varepsilon \geq 0$,

and if Φ^*_ε is the set of virtual mole fractions associated with the perturbed problem, there exists $\xi(\varepsilon) \in \Phi^*_\varepsilon$ such that:

(III.2.39) $\bar{\xi}_{<j>}(\varepsilon) < 1 \quad \forall\, j \in I \cup K.$

<u>Note</u>: The effect of this perturbation is to move each j originally in K to I.

<u>Proof</u>: To show (III.2.38) we note from (III.2.37) that since $x \geq 0$,

$$\bar{F}(x) = F(x) + \varepsilon \sum_{j \in K} x_j \geq F(x),$$

with equality if $x \in M(F|H)$ (since then $x_j = 0$ if $j \in K$).

Thus:

$$M(\overline{F}|H) = M(F|H).$$

To show (III.2.39), pick any $\xi \in \Phi^*$ (the set of virtual mole fractions associated with the unperturbed problem) satisfying:

$$\overline{\xi}_{<j>} < 1 \quad \text{for } j \in I.$$

Let $\xi(\varepsilon)$ be defined by:

$$\xi_j(\varepsilon) = \begin{cases} \xi_j & \text{if } j \in I \cup J \\ \xi_j e^{-\varepsilon} & \text{if } j \in K. \end{cases}$$

Clearly, for $j \in K$,

$$\overline{\xi}_{<j>}(\varepsilon) = e^{-\varepsilon} < 1.$$

It is trivial to check that $\xi(\varepsilon) \in \Phi^*_\varepsilon$. QED.

Again, it would be easy but pointless to prove that $\lim_{t \to 0^+} \hat{x}(t)$ is continuous as a function of the perturbation ε at $\varepsilon = 0$. (The reader is refered to Theorem III.2.2. Notice the similarity between this problem and that of proving $x^*_\delta \to x^*$, mentioned immediately before Lemma III.2.12.)

Experience has led the author to believe that the solution of the chemical equilibrium problem is continuous in nearly every conceivable perturbation, as one would expect of a physical system. Unfortunately a proof of the general statement that $x(t) \to x^*$ as $t \to 0$ has been elusive.

REFERENCES

1 Bigelow, J. H., "Chemistry, Kinetics, and Thermodynamics".

2 Duffin, R. J., E. L. Peterson & C. Zenner, Geometric Programming, John Wiley & Sons, 1967.

3 Hamala & Milan, "Geometric Programming in Terms of Conjugate Functions," Disc. Paper #6811, International Center for Management Science, Université Catholique de Lonvain, Belgium.

4 Bigelow, J. H., J. C. DeHaven & N. Z. Shapiro, Chemical Equilibrium Problems with Unbounded Constraint Sets, The RAND Corporation, RM-5952-PR, 1970. Also to appear in SIAM J. of Appl. Math.

5 Shapiro, N. Z. & L. S. Shapley, "Mass Action Laws and the Gibb's Free Energy Function," J. Soc. Indust. Appl. Math, Vol. 13, No. 2, 1965.

6 Dantzig, G. B., Linear Programming and Extensions, Princeton Press, 1963.

7 Bigelow, J. H., The Chemical Equilibrium Problem, Tech. Rep. #63-1, Operations Research House, Stanford University, 1968.

8 Dantzig, G. B., J. Folkman & N. Z. Shapiro, "On the Continuity of the Minimum Set of a Continuous Function," J. Math. Anal. & Appl. Vol. 17, No. 3, 1967.

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13. Abstract

A single- or multi-phase chemical equilibrium problem may be viewed as the problem of minimizing a particular nonlinear function (the free energy) of composition subject to the conditions that the composition variables be nonnegative and satisfy a system of linear equality constraints (the mass-balance laws). Because problems of this form occur in other than chemical problems (for example in connection with geometric programming problems), the phrase "chemical equilibrium problem" refers in this paper only to a particular nonlinear programming problem.

The free energy function is convex and homogeneous of degree one, which considerably simplifies the chemical equilibrium problem. However, as the amount of some composition variable approaches zero, the directional derivative of the free energy may become (in the limit) a nonlinear function of direction. Indeed, the derivative may be infinite. Since there are problems whose solutions include variables with value zero, it is necessary to derive methods for recognizing when a degenerate composition vector is a solution.

We point out that a composition vector solves a chemical equilibrium problem if and only if it satisfies the mass-balance constraints and the associated vector of concentrations satisfies certain optimality conditions. The concentration associated with a variable is the ratio of that variable to the sum of all variables in the same phase. Thus the concentrations of species of an empty phase are undefined. Even when some phases are empty, however, it is possible to define quantities to replace the missing concentrations.

An alternative method to handle degenerate problems is to add a minute amount of a nonreacting, nondiffusing substance to each phase. This perturbed problem will have a unique, nondegenerate solution whenever the set of solutions to the original problem is nonempty and bounded. The solution to the perturbed problem will be close to some solution to the original problem.

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14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

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